90-186689/25 E14 L03 (E13) MERE 25.11.89
MERCK PATENT GMBH *DE 3939-116-A
07.12.88-DE-841120 (+DE-9939116) (13.04.90) C07c-255/50
C07d-309/04 C07d-319 C07d-335/02 C07d-339 C09k-19/14

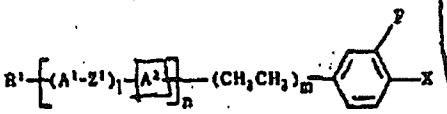
2-Fluoro-benzonitrile deriva. prodn. - by metallation of 3-substd. fluorobenzene(s), followed by carboxylation or formylation and conversion into nitrile

C90-080922

E(7-D5, 10-A15B, 10-A15D) L(3-D1D1)

L 0064

(1) 2-Fluorobenzonitrile derivs. (I) of formula (I) (X = CN) are produced by metallation of the corresp. fluorobenzene deriv. (II) (X = H) to form the corresp. metal deriv. (III) (X = Li, Na or K), then carboxylating (III) and converting the carboxylic acid into (I) or formulating (III) and converting the resulting aldehyde into (I).



(I)

R^1 = up to 18C perfluoroalkyl, alkyl or alkenyl (opt. with one or more CH_2 gps. replaced by O, S or $-C\equiv C-$; A^1, A^2 = (a) 1,4-phenylene, (b) 1,4-cyclohexylene (opt. with 1 or 2 non-adjacent CH_2 gps. replaced by O or S) or (c) 1,4-cyclohexenylene, 1,4-bicyclo-[2.2.2]octylene or piperidine-1,4-diyl (with (a) and (b) opt. mono- or poly-substd. with Hal and/or Me);

Z^1 = $-CH_2-CH_2-$, $-OCH_2-$, $-CH_2O-$ or single bond;

n = 0, 1 or 2; l,m = 0 or 1; l + m = 1, 2, 3 or 4.

(2) Cpds. (I) with A^1 = A^2 = 1,4-phenylene, Z^1 = $-CH_2-CH_2-$ or single bond, l = n = 1, m = 0 or 1 (if m = 0, then Z^1 = $-CH_2-CH_2-$) are claimed as such.

USE/ADVANTAGES

(I) are useful as intermediates, esp. for the synthesis of liq. crystalline cpds., or as components of liq.crystalline phases (to improve dielectric anisotropy or other properties). The invention provides a regiospecific process for the prodn. of (I) in good yield.

DETAIL

(III) is, e.g. 4-R^1-3'-fluorobiphenyl, 3-fluoro-4'-R^1-cyclohexylbenzene, etc. (14 R^1-substd. starting cpds.

DE3939116-A+

listed); metallation is carried out at -80 to -30°C with, e.g. n-BuLi, KNH_2 etc. in a solvent such as THF, dioxan, cyclohexane, toluene, etc. with HMPT etc. as activator.

EXAMPLE

10 ml. 0.1-M soln. of n-BuLi in hexane was added at -70°C to a mixt. of 0.1 mol. 3-(trans-4-heptylcyclohexyl)-fluorobenzene (prepd. as described in EP-119756) and 0.1 mol. tetramethylethylenediamine in 200 ml. THF, then the mixt. was stirred for 2 hrs. at -78°C, treated with a mixt. of 0.1 mol. N-formylpiperidine and 20 ml. THF, warmed to room temp. and worked up to give a solid prod.; 0.1 mol. of the aldehyde obtd. was reacted with 0.12 mol. hydroxylamine O-sulphonic acid as described in Helv.Chim.Acta 59, 2796 (1976) and worked up to give 4-(trans-4-heptylcyclohexyl)-2-fluorobenzonitrile as a colourless solid. The prod. had crystalline/nematic transition pt., 19°C; nematic/isotropic transition pt., 27°C. (10pp1712DWDwgNo0/0).

DE3939116-A

1990 DERWENT PUBLICATIONS LTD.